

Correlation of oxidation states of surface chromium species with ethylene polymerization activity for Phillips $\text{CrO}_x/\text{SiO}_2$ catalysts modified by Al-alkyl cocatalyst

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Received 12 January 2005; received in revised form 14 May 2005; accepted 16 May 2005

Available online 23 June 2005

Abstract

The real oxidation states of active sites on the important industrial Phillips type catalysts are still unclear. In this study, Phillips catalysts calcined at different temperatures (400, 600 and 800 °C) were modified by triethylaluminum (TEA) at different Al/Cr molar ratio and subsequently characterized by X-ray photoelectron spectroscopy (XPS) method and ethylene polymerization tests in order to elucidate the real oxidation states of active sites. Activity of each catalyst increases up to a maximum value then drops down with the increasing of Al/Cr molar ratio. The TEA-modified catalyst calcined at higher temperature got a larger maximum value of polymerization activity at a lower Al/Cr molar ratio. XPS method quantified the mixed Cr oxidation states including +2, +3, +5 and +6 of surface chromium species, in which only the +2 and +6 Cr species were found to be relating to the polymerization activity. The real active chromium precursor might be a chromium cluster (Scheme 1) named as $\text{Cr}^{2+} \cdot 2\text{Cr}^{6+}$ composed of one $\text{Cr}(\text{II})\text{O}_{x,\text{surf}}$ species and two $\text{Cr}(\text{VI})\text{O}_{x,\text{surf}}$ species, in which the former acts as the real center of active Cr cluster and the latter acts as the necessary neighboring ligand environment. The relative concentration of active sites is estimated to be around 14.4–24.9 (mol % Cr) for the TEA-modified Phillips catalysts depending on the calcination temperature and Al/Cr molar ratio.

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Keywords: Phillips $\text{CrO}_x/\text{SiO}_2$ catalyst; Ethylene polymerisation; Oxidation state; Surface chromium species; Triethylaluminum cocatalyst; XPS

1. Introduction

Supported chromium oxide catalysts are known to be widely applicable to various important industrial processes including hydrogenation, dehydrogenation and olefin polymerization [1–3]. As for olefin polymerization, Phillips $\text{CrO}_x/\text{SiO}_2$ catalysts are nowadays still responsible for nearly seven million tons of commercial polyolefin production covering more than one thirds of the world high density polyethylene (HDPE) market. The other remaining nearly two thirds of the world HDPE was made by Ziegler–Natta catalysts. Due to its lower cost and quite unique product properties originating from the unique microstructure of HDPE chain

with very broad molecular weight distribution and long chain branches, Phillips catalyst is still quite competitive against Ziegler–Natta catalyst especially in the application area of blow molding products [4,5]. However, in spite of more than half century of great research efforts, the states of the active sites and polymerization mechanism still remains unclear [6–9]. The real oxidation state, precise chemical structure and composition of the active sites are the most controversial problems, which hindered further development of this important commercial catalyst in both industrial field and academic circle [6–9]. This could explain well why Phillips $\text{CrO}_x/\text{SiO}_2$ catalyst is still extracting intensive research interests nowadays [10–18].

The application of the Phillips catalyst for ethylene polymerization includes two most important processes [7]. The first is a calcination process at high temperature (usually

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around 600–800 °C) for supporting the bulky CrO₃ onto the silica gel surface as chromate species. The surface physico-chemical nature and catalytic properties of the calcined catalyst significantly depend on the calcination conditions [7]. The second is a activation process for reducing of the chromate species into divalent Cr(II) site as the real active precursor for ethylene polymerization. The activation process could be performed by ethylene monomer, carbon monoxide (CO), metal-alkyl compounds, sometimes or even other reducing agents, respectively [7]. The calcination process with respect to surface physico-chemical nature and catalytic properties of the calcined Phillips catalysts [7,16–18], as well as the activation of Phillips catalysts by CO had been fully investigated [7,12,14,15], whereas, the activation of Phillips catalyst by either ethylene monomer or metal-alkyl compounds were scarcely reported in the literature. Recently, the activation mechanism by ethylene monomer was studied through probing the induction period of ethylene polymerization in our previous reports [19–22]. The induction period was found to be corresponding to not only reduction of chromate species but also ethylene metathesis through formation of chromium carbene species [21]. The subsequent ethylene polymerization was initiated through transformation of metathesis active sites into polymerization sites by desorption of the formaldehyde [22]. Regarding the activation of Phillips catalyst by metal-alkyl compounds, only a few publications could be found during the past several decades [23–30]. Spitz et al. reported the significant effect of even small amount of TEA on the activity, kinetics and 1-hexene incorporation for ethylene-1-hexene copolymerization in liquid 1-hexene using a Phillips catalyst [23]. McDaniel and Johnson studied about the effects of triethylborane (TEB) on the polymerization kinetics and chain transfer of Phillips catalyst using different supports (AlPO₄, SiO₂, Al₂O₃) [24,25]. Tait and co-authors presented a work using tri-isobutylaluminium (TIBA) for studies of its effects on kinetics and polymer morphology with Phillips CrO_x/SiO₂ catalyst [26]. Bade and Blom found two kinds of active sites on the lithium-alkyl modified Phillips CrO_x/SiO₂ catalyst including oligomerization sites and polymerization sites resulting in the formation of linear low density polyethylene (LLDPE) production due to the in situ incorporation of the α -olefin oligomers [27,28]. More recently, we have shown the plausible existence of two kinds of active sites for ethylene homo- and co-polymerization with 1-hexene using a CO-prereduced Phillips CrO_x/SiO₂ catalyst in the presence of TEA cocatalyst [29,30]. In general, it is evident that organo-metal compound can not only assist the active site formation through reduction and/or alkylation but also significantly affect the catalytic properties of the Phillips type catalysts, as well as the structures and the properties of the produced polymers, through ligand modification of active sites or even creation of completely new active sites. Unfortunately, very little information concerning the physico-chemical nature of surface chromium species on the organometal-modified Phillips type catalysts could be found in the literature. In our previous work [16–18],

the X-ray photoelectron spectroscopic (XPS) method had been demonstrated to be one of the most powerful methods for both qualitative and quantitative understanding the oxidation states of surface chromium species on Phillips CrO_x/SiO₂ catalysts, which had been widely used for characterization of various types of Cr-based catalysts in the literature [10,16–19,31–45]. However, it has never been utilized for investigation on organometal-modified Phillips type catalysts up to now. In this work, XPS method was applied to characterize the oxidation states of surface chromium species on Phillips CrO_x/SiO₂ catalysts modified by TEA cocatalyst under different Al/Cr molar ratios [46]. The XPS data were further correlated with the results of ethylene polymerization activity in order to get deeper understanding on the nature of active chromium species on these TEA-modified Phillips CrO_x/SiO₂ catalysts.

2. Experimental

2.1. Raw materials

Nitrogen of G2-grade (total impurity <2 ppm, in which O₂ <0.3 ppm, CO <0.3 ppm, CO₂ <0.3 ppm, CH₄ <0.1 ppm, NO_x <0.1 ppm, SO₂ <0.1 ppm, dew point of H₂O <–80 °C), and pure air of G1-grade (total impurity <1 ppm, CO <0.1 ppm, CO₂ <0.1 ppm, THC <0.1 ppm, NO_x <0.01 ppm, SO₂ <0.01 ppm, dew point of H₂O <–80 °C) were purchased from Uno Sanso Co. Ethylene of research grade (C₂H₄ >99.9%, air <0.03%, methane <0.01%, ethane <0.05%, propane <0.01%, analyzed by Gas Chromatography method) was donated by Mitsubishi Chemical Co. Molecular sieves 4A and molecular sieves 13X, which were purchased from Wako Pure Chemical Industries Ltd., were used as moisture scavenger for gas purification. Q-5 reactant catalyst (13 wt.% of copper (II) oxide on alumina), which was purchased from Aldrich, was used as oxygen scavenger for gas purification. A catalyst precursor of Crosfield ES370 with 1.0 wt.% of Cr loading and surface area of 280–350 m²/g, which was donated from Asahi Kasei Co., was used for preparation of Phillips CrO_x/SiO₂ catalyst calcined at various temperatures. Triethylaluminum (TEA, donated by Tosoh Fine Chem. Co.) was used without further purification. TEA was used as heptane solution. Heptane (purchased from Wako Pure Chemical Industries, Ltd.) was purified by passing through a column of molecular sieves 13X and subsequently purged by pure nitrogen bubbling flow for more than 2 h before use. CCl₄ was also purchased from Wako Pure Chemical Industries Ltd.

2.2. Catalyst preparation

The details about catalyst preparation of the calcined Phillips catalyst could be found in our previous report [17,18,29]. A simplified introduction of catalyst preparation process was given as follows. About 15 g of catalyst

precursor was added into a spouted fluidized-bed quartz reactor followed by an isothermal calcination process at a certain temperature (400, 600 or 800 °C) in pure air with a flow rate of 200 ml/min for 6 h. Dry air was further purified by passing through a 13X molecular sieve column before entering the catalyst preparation system. The calcined catalyst was cooled down to room temperature in nitrogen (200 ml/min). Nitrogen was further purified by passing through a Q-5 catalyst column and a 13X molecular sieve column before entering the catalyst preparation system. Three calcined Phillips catalysts named as PC400, PC600 and PC800 calcined at 400, 600 and 800 °C, respectively, were prepared for further modification by TEA cocatalyst. Each catalyst was modified by TEA before using for polymerization. The modification was carried out under nitrogen atmosphere in a glass reactor connected to a high vacuum line. The reactor was filled with 30 ml of heptane and about 1 g of calcined catalyst, thereafter a controlled amount of TEA was added according to different Al/Cr molar ratio. The mixture was allowed to react for 30 min at room temperature. Solution was decanted before drying of the modified catalyst by vacuum. Each TEA-modified catalyst was further distributed and sealed in many small glass ampoule bottles and the amount of catalyst in each ampoule bottle was regulated to about 100 mg, which was weighed precisely. The TEA-modified catalysts could be divided into three categories according to the calcination temperatures of the original calcined catalysts named as PC400/TEA, PC600/TEA and PC800/TEA, respectively.

2.3. Characterization of catalysts

XPS data for the TEA-modified catalysts were obtained on a Physical Electronics Perkin-Elmer Model Phi-5600 ESCA spectrometer with monochromated Al K α radiation (1486.6 eV) operated at 300 W. The detailed procedure could be found in our previous reports [16]. Each catalyst sample was embedded on a conductive copper tape fixed on a sample holder. The sample holder was then put into a transfer vessel (Phi Model 04-110, Perkin-Elmer Co. Ltd.), which can be connected to the sample introduction chamber on the XPS instrument for the inert atmospheric sample transfer. The prepared sample was degassed in the introduction chamber to 10^{-7} torr before entering the main chamber, in which the vacuum was kept under 3×10^{-9} torr during the 2 h XPS data acquisition. A neutralizer was used to reduce the charging effect to obtain a better signal to noise ratio. The X-ray irradiation-induced reduction of Cr species for these partially-reduced TEA-modified Phillips catalysts was found to be negligible during the XPS measurement within 2 h. All binding energies were referenced to the Si 2p peak of silica gel at 103.3 eV to correct for charging. Multiplet fitting of the Cr 2p XPS curves by the Gaussian–Lorentzian method was conducted after the measurement to obtain the precise oxidation states of surface chromium species in each TEA-modified catalyst. The fitting for each curve was repeated for several times to ensure a reproducible result.

IR spectra of the original calcined catalysts and several TEA-modified catalysts were obtained on an apparatus Perkin-Elmer 330. Each catalyst sample was transferred into a quartz cell of 1 cm thickness containing purified CCl₄ as a medium and measurement was carried out in the range of 4000–8000 cm⁻¹. The band at 4425 and 7140 cm⁻¹ was used for qualitative analysis of the relative amount of residual surface hydroxyl groups between different samples according to the literature [47,48].

2.4. Ethylene polymerization

The same experimental system for semi-batch slurry ethylene polymerization used in our previous report was utilized [29]. One ampoule bottle with ca. 100 mg of TEA-modified catalyst was set in the top part of the glass polymerization reactor (volume ca.100 ml). Then, the reactor system was heated and vacuumed for 2 h before introduction of heptane and ethylene. The polymerization was initiated after breaking of the catalyst ampoule bottle by a steel bar. Ethylene was further purified by passing through a 4A molecular sieve column, a Q-5 catalyst column and a 13X molecular sieve column before entering the polymerization system. The polymerization conditions are shown as follows: ethylene pressure 0.15 MPa, polymerization temperature: 60 °C, 20 ml heptane. The real time ethylene consumption was continuously monitored by an on-line mass flowmeter. The polymerization was stopped by adding 20 ml ethanol/HCl after 1 h. The polymer was washed and dried in vacuum at 60 °C for 6 h.

3. Results and discussion

The oxidation states of surface chromium species on the three original calcined Phillips CrO_x/SiO₂ catalysts (PC400, PC600 and PC 800) isothermally calcined at 400, 600 and 800 °C, respectively, had already been fully investigated by XPS method in our previous work [17]. It has been made clear that PC400 contains 100% of chromate species (Cr(VI)O_{x,surf}) with a binding energy (BE) of 580.7 eV, PC600 contains 96.9% of Cr(VI)O_{x,surf} with a BE of 581.0 eV and 3.1% of Cr(III)O_{x,surf} species with a BE of 577.6 eV, and PC800 contains 95.0% of Cr(VI)O_{x,surf} with a BE of 581.9 eV and 5.0% of Cr(III)O_{x,surf} species with a BE of 577.7 eV [17]. In this work, the PC400, PC600 and PC800 catalysts were further modified by TEA cocatalyst at various Al/Cr molar ratios before XPS measurements and ethylene homo-polymerization. The oxidation states of surface chromium species on the TEA-modified catalysts (including three groups of catalysts: PC400/TEA, PC600/TEA and PC800/TEA catalysts) were correlated with the polymerization activity in terms of calcination temperature and Al/Cr molar ratio in order to get clearer understanding concerning the valent state of the real active precursor on the TEA-modified Phillips CrO_x/SiO₂ catalysts.

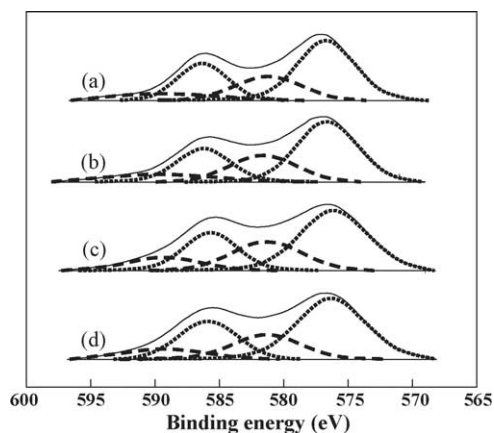


Fig. 1. Cr 2p XPS spectra of the TEA-modified Phillips catalysts calcined at 400 °C (high resolution XPS acquisition time 2 h for all spectra) in different Al/Cr molar ratios: (a) 3.12; (b) 5.20; (c) 6.24; and (d) 7.28.

The Cr 2p XPS spectra of the PC400/TEA, PC600/TEA and PC800/TEA catalysts were shown in Figs. 1–3, respectively. A single doublet fitting for the spectra of all the TEA-modified catalysts was found to be impossible in order to get a perfect curve fitting, which indicated that multiple oxidation states of surface chromium species existed in each catalyst. Multiplet fittings of the Cr 2p XPS curves by the Gaussian–Lorentzian method were carried out to determine the mixed valence states in all the samples through peak deconvolution as shown by the peaks in dot or dash lines in each spectrum in Figs. 1–3. For each deconvoluted peak from the Cr2p (3/2) level at the low binding energy side, there is a corresponding peak with half peak area at the high binding energy side, which is from the Cr2p (1/2) level of the same Cr oxidation state. The assignments of oxidation states of chromium components in each sample were based on the binding energy values from the

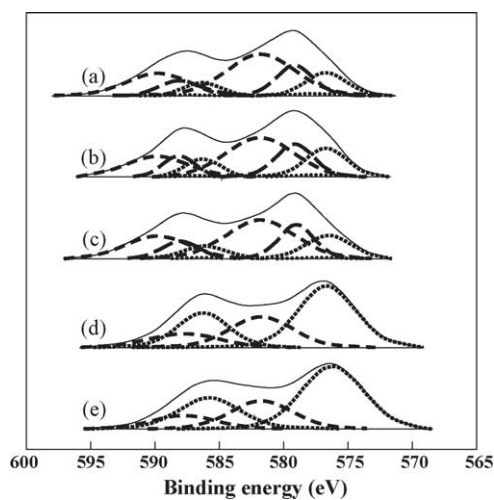


Fig. 2. Cr 2p XPS spectra of the TEA-modified Phillips catalysts calcined at 600 °C (high resolution XPS acquisition time 2 h for all spectra) in different Al/Cr molar ratios: (a) 2.08; (b) 3.12; (c) 4.16; (d) 5.20; and (e) 6.24.

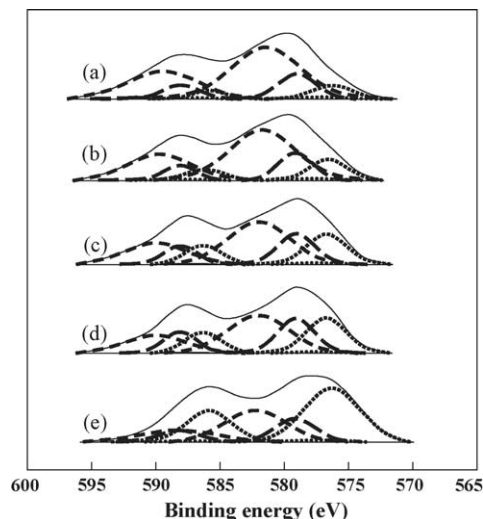


Fig. 3. Cr 2p XPS spectra of the TEA-modified Phillips catalysts calcined at 800 °C (high resolution XPS acquisition time 2 h for all spectra) in different Al/Cr molar ratios: (a) 1.56; (b) 2.34; (c) 2.86; (d) 3.12; and (e) 3.64.

Cr2p (3/2) level according to the literature and our previous reports [10,16–19,31–45]. For examples, chromium component with a BE around 580.7–581.9 eV from the Cr2p (3/2) level was assigned to chromate species ($\text{Cr(VI)O}_{x,\text{surf}}$) [10,16–19,35,41]. Chromium component with a BE around 576.0–576.6 eV from the Cr2p (3/2) level was assigned to $\text{Cr(II)O}_{x,\text{surf}}$ species [19,35]. Chromium component with a BE around 577.0–577.6 eV from the Cr2p (3/2) level was assigned to $\text{Cr(III)O}_{x,\text{surf}}$ species [16–19,35]. The BE value from the Cr2p (3/2) level for bulky pentavalent chromium oxide is reported to be around 577.5–577.8 eV [17,33]. Therefore, it is reasonable to assign chromium component with a BE around 578.5–578.8 eV from the Cr2p (3/2) level to $\text{Cr(V)O}_{x,\text{surf}}$ species due to the supporting effect from the silica gel surface [16]. Accordingly, atomic percentage of each oxidation state of surface chromium species on PC400/TEA, PC600/TEA and PC800/TEA catalysts were obtained and shown in Tables 1–3, respectively.

The XPS characterization revealed the existence of two oxidation states Cr^{2+} ($\text{Cr(II)O}_{x,\text{surf}}$) and Cr^{6+} ($\text{Cr(VI)O}_{x,\text{surf}}$) of surface chromium species on the PC400/TEA catalysts as shown in Tab.1. The atomic percentages of Cr^{2+} ($\text{Cr(II)O}_{x,\text{surf}}$) and Cr^{6+} ($\text{Cr(VI)O}_{x,\text{surf}}$) on PC400/TEA

Table 1
Relationship of Cr oxidation states vs. ethylene polymerization activity for the PC400/TEA catalysts in terms of Al/Cr molar ratio

Al/Cr molar ratio	Atomic percentage (%) ^a				Activity (gPE/gcat·[C ₂ H ₄]-h)
	Cr ²⁺	Cr ³⁺	Cr ⁵⁺	Cr ⁶⁺	
3.12	69.6	0	0	30.4	330
5.20	68.1	0	0	31.9	760
6.24	67.9	0	0	32.1	770
7.28	71.1	0	0	28.9	560

^a Measured by XPS method.

Table 2

Relationship of Cr oxidation states vs. ethylene polymerization activity for the PC600/TEA catalysts in terms of Al/Cr molar ratio

Al/Cr molar ratio	Atomic percentage (%) ^a				Activity (gPE/gcat·[C ₂ H ₄]-h)
	Cr ²⁺	Cr ³⁺	Cr ⁵⁺	Cr ⁶⁺	
2.08	18.6	2.1	22.4	56.9	680
3.12	23.5	1.8	24.8	49.9	878
4.16	25.6	1.3	23.6	49.5	1560
5.20	65.0	0	0	35.0	960
6.24	69.4	0	0	30.6	940

^a Measured by XPS method.

catalysts were around 67.9–71.1% and 28.9–32.1%, respectively, without showing significant dependence on the Al/Cr molar ratios ranging from 3.12 to 7.28. It was made clear that more than two-thirds of the Cr(VI)O_{x,surf} species on PC400 were reduced into Cr(II)O_{x,surf} species after modified by TEA without obvious variation when changing Al/Cr molar ratios from 3.12 to 7.28. On the other hand, the PC600/TEA and PC800/TEA catalysts showed much more complicated oxidation states including Cr²⁺ (Cr(II)O_{x,surf}), Cr³⁺ (Cr(III)O_{x,surf}), Cr⁵⁺ (Cr(V)O_{x,surf}) and Cr⁶⁺ (Cr(VI)O_{x,surf}) of surface chromium species and much more sensitive dependence on the Al/Cr molar ratios as shown in Tables 2 and 3, respectively. Moreover, the sensitivities of dependence of atomic percentages for chromium valent components especially Cr²⁺ and Cr⁶⁺ on Al/Cr molar ratio seem increase with increasing calcination temperature. The atomic percentages of Cr²⁺ (Cr(II)O_{x,surf}) on PC600/TEA catalysts increased from 18.6 to 69.4% and simultaneously the atomic percentages of Cr⁶⁺ (Cr(VI)O_{x,surf}) on PC600/TEA catalysts decreased from 56.9 to 30.6% as the Al/Cr molar ratios increased from 2.08 to 6.24. The atomic percentages of Cr³⁺ (Cr(III)O_{x,surf}) and Cr⁵⁺ (Cr(V)O_{x,surf}) on PC600/TEA catalysts were around 1.3–2.1% and 22.4–24.8%, respectively, without showing obvious dependence when the Al/Cr molar ratios increase from 2.08 to 4.16, and suddenly decrease to zero at Al/Cr molar ratios of 5.20 and 6.24. As for the PC800/TEA catalysts, similar tendencies could be observed for dependences of atomic percentages of Cr²⁺ (Cr(II)O_{x,surf}) and Cr⁶⁺ (Cr(VI)O_{x,surf}) on the Al/Cr molar ratios. The atomic percentages of Cr²⁺ (Cr(II)O_{x,surf}) on PC800/TEA catalysts increased from 10.1 to 50.1% and simultaneously the atomic percentages of Cr⁶⁺ (Cr(VI)O_{x,surf}) on PC800/TEA catalysts

Table 3

Relationship of Cr oxidation states vs. ethylene polymerization activity for the PC800/TEA catalysts in terms of Al/Cr molar ratio

Al/Cr molar ratio	Atomic percentage (%) ^a				Activity (gPE/gcat·[C ₂ H ₄]-h)
	Cr ²⁺	Cr ³⁺	Cr ⁵⁺	Cr ⁶⁺	
1.56	10.1	2.1	18.1	69.7	610
2.34	15.3	1.9	17.4	65.4	878
2.86	24.9	1.7	22.9	50.5	1838
3.12	28.4	1.5	26.0	44.1	1203
3.64	50.1	1.6	16.5	31.8	1123

^a Measured by XPS method.

decreased from 69.7 to 31.8% as the Al/Cr molar ratios increased from 1.56 to 3.64. The atomic percentages of Cr³⁺ (Cr(III)O_{x,surf}) and Cr⁵⁺ (Cr(V)O_{x,surf}) on PC800/TEA catalysts were around 1.5–2.1% and 16.5–26.0%, respectively, without showing obvious dependence and tendency when the Al/Cr molar ratios increase from 1.56 to 3.64. Up to now, a precise quantitative understanding of the mixed oxidation states of various surface chromium species on the TEA-modified Phillips catalysts in terms of calcination temperatures and Al/Cr molar ratios had been demonstrated in the present work. In general, the sensitivity dependence of content variation of surface chromium species in different oxidation states especially for Cr²⁺ (Cr(II)O_{x,surf}) and Cr⁶⁺ (Cr(VI)O_{x,surf}) on Al/Cr molar ratio for the TEA-modified Phillips catalysts increases with increasing of calcination temperature, and thus much lower Al/Cr molar ratio is needed for the activation of Phillips catalysts calcined at higher calcination temperature by TEA cocatalyst for ethylene polymerization, which will be discussed in details through correlation of these quantified oxidation states of surface chromium species with ethylene polymerization activity in the following section.

Ethylene homo-polymerizations using the TEA-modified Phillips catalysts were performed and the polymerization activities for PC400/TEA, PC600/TEA and PC800/TEA catalysts were shown in Tables 1–3, respectively. The dependences of polymerization activities on Al/Cr molar ratios and calcination temperatures were also plotted in Fig. 4. The polymerization kinetics for all the TEA-modified catalysts were found to be the same typical kinetics form as TiCl₃/TEA and metallocene catalysts, in which the polymerization rate was built-up quickly from zero to a maximum within several to 30 min followed by gradual decrease to stationary rate. As an example, three real time profiles of ethylene homo-polymerization kinetics using the PC600/TEA catalysts prepared at different Al/Cr molar ratios of 2.08, 3.12, and 4.16, respectively, were shown in Fig. 5. This type of kinetics for TEA-modified Phillips CrO_x/SiO₂ catalysts is consistent with those reported by Spitz et al. [23] and McDaniel et al. [24] using a Cr/SiO₂/TEA and Cr/AlPO₄/TEB catalyst,

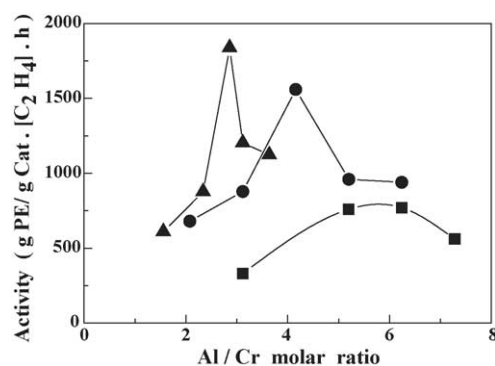


Fig. 4. Al/Cr molar ratio versus polymerization activity for the TEA-modified Phillips catalysts calcined at 400 °C (■); 600 °C (●); and 800 °C (▲).

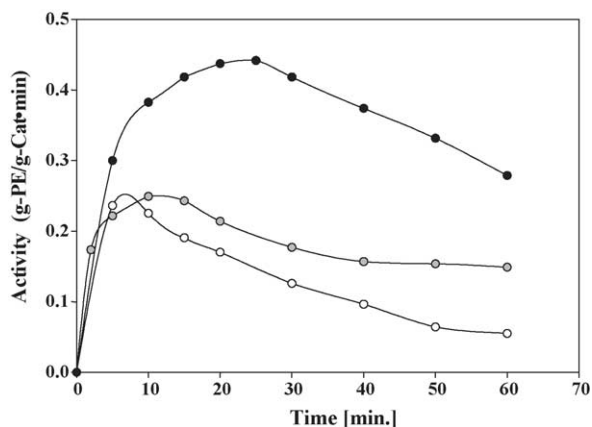
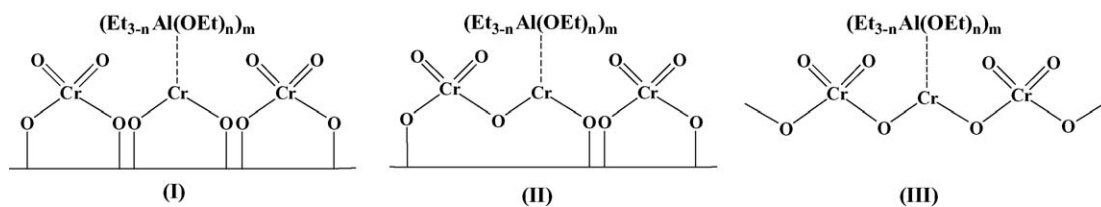


Fig. 5. The real time profiles of ethylene homo-polymerization kinetics with the 600 °C-calcined Phillips catalyst modified by TEA cocatalyst at different Al/Cr molar ratios: 2.08 (○); 3.12 (○●); and 4.16 (●).

respectively. As it can be seen from Tables 1–3 and Fig. 4, PC400/TEA catalysts showed much lower polymerization activity than the PC600/TEA and PC800/TEA catalysts. The average activity of the PC800/TEA catalysts is slightly higher than that of the PC600/TEA catalysts. It is most interesting to notice that sensitivity of dependence of variation in polymerization activity on Al/Cr molar ratio is similar to sensitivity of dependence of variation in chromium oxidation states on Al/Cr molar ratio for PC400/TEA, PC600/TEA and PC800/TEA catalysts, respectively. In other words, corresponding to the fact that the sensitivity dependence of content variation of surface chromium species in different oxidation states especially for Cr^{2+} ($\text{Cr(II)O}_{x,\text{surf}}$) and Cr^{6+} ($\text{Cr(VI)O}_{x,\text{surf}}$) on Al/Cr molar ratio for the TEA-modified Phillips catalysts increases with increasing of calcination temperature, the sensitivity dependence of activity variation of TEA-modified Phillips catalysts on Al/Cr molar ratio also increases with increasing of calcination temperature. It was clearly demonstrated in Fig. 4 that PC400/TEA catalysts showed the lowest sensitivity in dependence of polymerization activity on Al/Cr molar ratio in comparison with PC600/TEA and PC800/TEA catalysts and PC800/TEA catalysts showed the highest sensitivity in dependence of polymerization activity on Al/Cr molar ratio. The activities of all three types of catalysts firstly increase with increase of Al/Cr molar ratio and then reach a maximum value followed by a decreasing of activity with further increase of Al/Cr molar ratio. The Al/Cr molar ratio for obtaining maximum activity decreases from 6.24 to 4.16 and 2.86 for PC400/TEA, PC600/TEA and PC800/TEA catalysts, respectively. Correspondingly, the maximum activity increases from 770 to 1560 and 1838 gPE/gcat·[C₂H₄]_h for PC400/TEA, PC600/TEA and PC800/TEA catalysts, respectively.

Further correlation of polymerization activities with oxidation states of surface chromium species based on the results shown in Tables 1–3 was considered in order to elucidate what's the oxidation state of the real active precursor within all surface chromium species on TEA-modified Phillips cat-

alysts, which is still ambiguous and open for discussion. For Phillips catalysts activated by ethylene monomer or CO, almost all Cr oxidation states including +2, +3, +4, +5 and +6 had been ever proposed to be plausible for the active sites of polymerization in the literature [7]. Within recent decades, it became widely accepted that divalent $\text{Cr(II)O}_{x,\text{surf}}$ species might be the final real active Cr precursor on the activated Phillips catalysts by ethylene monomer or CO although the oxidation state of active site during polymerization might be changed into +3 or +4 after alkylation of the active $\text{Cr(II)O}_{x,\text{surf}}$ precursor by ethylene monomer [6–9,13–15,35]. Up to now, almost no such effort has been put to the Phillips catalysts activated by Al-alkyl cocatalyst most probably due to the complexity coming from the activation power of Al-alkyl cocatalyst capable of not only reduction but also alkylation as shown in the Ziegler–Natta catalyst systems. According to our results regarding the oxidation states of surface chromium species and polymerization activities for the TEA-modified Phillips catalysts as shown in Tables 1–3, the surface chromium species in oxidation states of +3 and +5 showed no direct relationship with the polymerization activity and thus could be ruled out as the active Cr precursor. It seems only the surface chromium species in oxidation states of +2 and +6 are possibly related with the activity of the catalysts for ethylene polymerization. The surface chromium species in oxidation state of +6 is chromate species from the original calcined Phillips catalysts. The chromate species is difficult to act as active Cr precursor for polymerization taking into account of its too low coordination ability to provide at least two extra coordination vacancies for monomer coordination and chromium carbon bond formation, which is the same as the Phillips catalysts activated by ethylene monomer or CO [6–9,13–15,35]. The $\text{Cr(II)O}_{x,\text{surf}}$ species in oxidation state of +2 is the only newly-formed surface chromium species, which can be found on all the TEA-modified Phillips catalysts, suggesting that it might be the most plausible real active chromium precursor on the TEA-modified Phillips catalysts for ethylene polymerization. The remaining question is “what's the role of the residual chromate species in oxidation state of +6?” for the TEA-modified Phillips catalysts in ethylene polymerization. According to Tables 2 and 3, polymerization activity for PC600/TEA and PC800/TEA catalysts increases proportionally with increasing of atomic percentage of $\text{Cr(II)O}_{x,\text{surf}}$ species at the region of low content of $\text{Cr(II)O}_{x,\text{surf}}$ species and high content of residual $\text{Cr(VI)O}_{x,\text{surf}}$ species. However, it decreases with the further increasing of atomic percentage of $\text{Cr(II)O}_{x,\text{surf}}$ species at the region of high content of $\text{Cr(II)O}_{x,\text{surf}}$ species and low content of residual $\text{Cr(VI)O}_{x,\text{surf}}$ species. This is also true for PC400/TEA catalysts, which show very low activity with high content of $\text{Cr(II)O}_{x,\text{surf}}$ species and low content of residual $\text{Cr(VI)O}_{x,\text{surf}}$ species. These evidences indicate that the real active chromium precursor on the TEA-modified Phillips catalysts might be a chromium cluster composed of both $\text{Cr(II)O}_{x,\text{surf}}$ and $\text{Cr(VI)O}_{x,\text{surf}}$ species, in which $\text{Cr(II)O}_{x,\text{surf}}$ species acts as the real center of active chromium



Scheme 1. Three plausible structure models of the active Cr^{2+} precursors existing as $\text{Cr}^{2+}\cdot 2\text{Cr}^{6+}$ cluster on the TEA-modified Phillips catalysts, $n = 1$, or 2, $m = 1$, or 2.

Table 4

Correlation of possible maximum concentration of active Cr^{2+} in $\text{Cr}^{2+}\cdot 2\text{Cr}^{6+}$ cluster with ethylene polymerization activity for the Phillips catalysts modified by TEA cocatalyst

Catalysts	Al/Cr molar ratio	Total Cr^{2+} (mol%)	Total Cr^{6+} (mol%)	Cr^{2+} in $\text{Cr}^{2+}\cdot 2\text{Cr}^{6+}$ (mol%) ^a	Activity (gPE/gcat·[C ₂ H ₄]-h)
PC400/TEA	3.12	69.6	30.4	15.2	330
	5.20	68.1	31.9	16.0	760
	6.24	67.9	32.1	16.1	770
	7.28	71.1	28.9	14.4	560
PC600/TEA	2.08	18.6	56.9	18.6	680
	3.12	23.5	49.9	23.5	878
	4.16	25.6	49.5	24.8	1560
	5.20	65.0	35.0	17.5	960
	6.24	69.4	30.6	15.3	940
PC800/TEA	1.56	10.1	69.7	10.1	610
	2.34	15.3	65.4	15.3	878
	2.86	24.9	50.5	24.9	1838
	3.12	28.4	44.1	22.0	1203
	3.64	50.1	31.8	15.9	1123

^a Calculated from the total contents of Cr^{2+} and Cr^{6+} on each TEA-modified catalyst based on the $\text{Cr}^{2+}\cdot 2\text{Cr}^{6+}$ cluster model.

precursor and the residual $\text{Cr}(\text{VI})\text{O}_{x,\text{surf}}$ species is also necessary component acting as the neighboring ligand environment with electronic and steric effects on the center of $\text{Cr}(\text{II})\text{O}_{x,\text{surf}}$ species. The optimal composition of this chromium cluster as the real active chromium precursor can be found to be composed of one $\text{Cr}(\text{II})\text{O}_{x,\text{surf}}$ species and two $\text{Cr}(\text{VI})\text{O}_{x,\text{surf}}$ species, which can be deduced from the $\text{Cr}^{2+}/\text{Cr}^{6+}$ molar ratio of approximate 1:2 in obtaining maximum polymerization activity for both PC600/TEA and PC800/TEA catalysts as shown in Tables 2 and 3. The active precursor of chromium cluster can be named as $\text{Cr}^{2+}\cdot 2\text{Cr}^{6+}$ cluster composed of one $\text{Cr}(\text{II})\text{O}_{x,\text{surf}}$ species and two $\text{Cr}(\text{VI})\text{O}_{x,\text{surf}}$ species. Three plausible chemical structural models of the $\text{Cr}^{2+}\cdot 2\text{Cr}^{6+}$ cluster are proposed in Scheme 1 based on our previous understanding of the surface chemical nature on calcined Phillips $\text{Cr}(\text{VI})\text{O}_x/\text{SiO}_2$ catalysts [16–18] as well as reduced Phillips $\text{Cr}(\text{II})\text{O}_x/\text{SiO}_2$ catalysts [19,20,22,29,30]. Model (I) of the $\text{Cr}^{2+}\cdot 2\text{Cr}^{6+}$ cluster derives from three neighboring monochromate species with the central one reduced into $\text{Cr}(\text{II})\text{O}_{x,\text{surf}}$ species by TEA. Model (II) originates from one dichromate species with one neighboring monochromate species as one of the Cr^{6+} was reduced into $\text{Cr}(\text{II})\text{O}_{x,\text{surf}}$ species by TEA. Model (III) might come from three neighboring Cr^{6+} in one polychromate species as the central Cr^{6+} was reduced into $\text{Cr}(\text{II})\text{O}_{x,\text{surf}}$ species by TEA. In all three cluster models, Al-alkoxyl byproduct from the reduction reaction

was supposed to be coordinated to the $\text{Cr}^{2+}(\text{Cr}(\text{II})\text{O}_{x,\text{surf}})$ center [24,29]. According to these active precursor models of $\text{Cr}^{2+}\cdot 2\text{Cr}^{6+}$ cluster, the possible maximum content of active Cr^{2+} precursor existing in $\text{Cr}^{2+}\cdot 2\text{Cr}^{6+}$ cluster could be calculated based on the total contents of Cr^{2+} and Cr^{6+} on each TEA-modified catalyst. The calculated results are shown in Table 4 and Fig. 6. A comparison between Fig. 6 and Fig. 4 indicates that a perfect correlation of polymerization activity with the content of active Cr^{2+} precursor existing in $\text{Cr}^{2+}\cdot 2\text{Cr}^{6+}$ cluster has been demonstrated. The relative

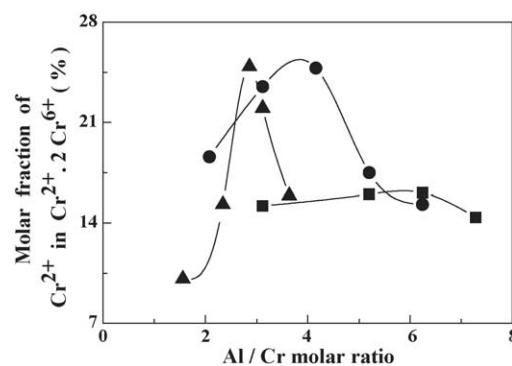


Fig. 6. Al/Cr molar ratio vs. the molar fraction of Cr^{2+} in $\text{Cr}^{2+}\cdot 2\text{Cr}^{6+}$ cluster on the TEA-modified Phillips catalysts calcined at 400 °C (■); 600 °C (●); and 800 °C (▲).

concentration of active sites according to the $\text{Cr}^{2+} \cdot 2\text{Cr}^{6+}$ cluster models is around 14.4–24.9 (mol% Cr) for TEA-modified Phillips catalysts (Table 4), which is comparable with 25% (mol% Cr) of relative active sites concentration for a CO-reduced Phillips $\text{Cr(II)O}_x/\text{SiO}_2$ catalyst obtained by in situ XANES/EXAFS method recently reported by Zecchina and co-authors [15]. They have also shown that the residual 50–75% of Cr^{2+} sites were not active for ethylene polymerization depending on the polymerization temperature [15]. From Table 4, it is also interesting to notice that with the same level of concentration of active Cr^{2+} precursor existing as $\text{Cr}^{2+} \cdot 2\text{Cr}^{6+}$ cluster for catalysts calcined at different temperatures usually the catalyst calcined at higher temperature show much higher polymerization activity. This could be rationalized well based on two factors affecting the nature of catalysts calcined at different temperatures. The first factor is the different amount of residual hydroxyl groups on original calcined PC400, PC600 and PC800 catalysts. As confirmed by our IR characterizations, the residual hydroxyl groups gradually decrease from PC400 to PC600 and PC800 catalysts. This is consistent with the long-standing experimental fact for silica gel and silica gel supported catalysts that the higher the calcination temperature leads to the lower amount of surface residual hydroxyl groups [7,49]. Moreover, these residual hydroxyl groups could not be completely removed through reaction with TEA most probably due to steric hindrance. This was further verified by IR measurements that the lower calcination temperature and the lower Al/Cr molar ratio will lead to the larger amount of surface residual hydroxyl groups after TEA modification. These residual hydroxyl groups are known to be poisonous to the active sites of Phillips type catalysts [7,50,51]. The second factor is relating to the intrinsic electronic state in terms of higher electron deficiency for chromate species ($\text{Cr(VI)O}_{x,\text{surf}}$) of the original Phillips catalysts calcined at higher temperatures as confirmed in our previous work [17], which might affect the electron deficiency of the $\text{Cr(II)O}_{x,\text{surf}}$ species reduced from $\text{Cr(VI)O}_{x,\text{surf}}$ species on the correlative TEA-modified Phillips catalysts.

4. Conclusions

In this work, oxidation states of surface chromium species on various TEA-modified Phillips $\text{CrO}_x/\text{SiO}_2$ catalysts (PC400/TEA, PC600/TEA and PC800/TEA catalysts) and their ethylene homo-polymerization activity in terms of catalyst calcination temperature (400, 600 and 800 °C) and Al/Cr molar ratio (1.56–7.28) have been investigated by XPS and semi-batch slurry polymerization methods, respectively. Subsequently, the quantified oxidation states of surface chromium species were correlated to polymerization activities. Polymerization kinetics for all TEA-modified catalysts were found to show the same typical kinetics form, in which the polymerization rate was built-up quickly from zero to a maximum followed by gradual decrease to stationary rate. The activities of all types of catalysts firstly increase with

increase of Al/Cr molar ratio and then reach a maximum value followed by a decreasing of activity with further increase of Al/Cr molar ratio. The sensitivity in dependence of polymerization activity on Al/Cr molar ratio increases with increasing calcination temperature. XPS method quantified the existence of four oxidation states including +2, +3, +5 and +6 of surface Cr species, in which only the +2 and +6 Cr oxidation states were relating to polymerization activity. Further evidences indicate that the real active chromium precursor on the TEA-modified Phillips catalysts might be a chromium cluster (Scheme 1) named as $\text{Cr}^{2+} \cdot 2\text{Cr}^{6+}$ composed of one $\text{Cr(II)O}_{x,\text{surf}}$ species and two $\text{Cr(VI)O}_{x,\text{surf}}$ species, in which $\text{Cr(II)O}_{x,\text{surf}}$ species acts as the real center of active chromium precursor and the residual $\text{Cr(VI)O}_{x,\text{surf}}$ species is also necessary component acting as the neighboring ligand environment with electronic and steric effects. Based on the $\text{Cr}^{2+} \cdot 2\text{Cr}^{6+}$ cluster models, the relative concentration of active sites is supposed to be around 14.4–24.9 (mol% Cr) for the TEA-modified Phillips catalysts depending on the calcination temperature and Al/Cr molar ratio.

Acknowledgements

The authors appreciate Toho Catalyst Co., Mitsubishi Chemical Co., and Tosoh Finechem. Co. for their support and donation to our laboratory.

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